Original Article

Geology and Geochemistry of the Germanium Deposits in Mainland China

Jian Zhao Yin[1] Ⓛ

Abstract

Thanks to China's unique geological settings, such as its location at the intersection of the Indian, Eurasian, and Pacific tectonic plates, it possesses a wealth of rare earth elements and rare metals, making it virtually unparalleled globally. In today's society, where cutting-edge technologies heavily rely on various critical metals, this natural advantage is highly significant. However, for various reasons, the outside world is not fully aware of many of China's dispersed metal resources. This paper introduces the uses and resource overview of germanium (Ge), one of many critical mineral resources in mainland China, and summarizes its spatial and temporal distribution within the country, classifying its industrial and genetic types, and discussing the geology and geochemistry of various associated/symbiotic Ge deposits. China has a wide variety of associated/symbiotic Ge deposits of various genesis, including endogenic igneous mesothermal-epithermal deposits, as well as skarn, porphyry, and volcanic deposits. There are also mixed igneous-aqueous hydrothermal deposits, such as volcanic-sedimentary deposits, formed by the combined effects of endogenic and exogenic geological processes. Of course, as a major coal-producing country, mainland China also possesses numerous organic and inorganic sedimentary associated/symbiotic Ge deposits, such as coal-type, phosphate-type, and bauxite-type deposits. These internal and external associated/symbiotic Ge deposits on the mainland are not completely isolated but rather mutually reinforcing. For example, organic coal-type Ge mineralization involves, to some extent, igneous magmatic activity, such as providing ore-forming materials.

Keywords: Type, germanium (Ge) mineralization, rare metal, spatiotemporal distribution, geology and geochemistry, mainland China

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Affiliation Info: 1 College of Earth Sciences, Jilin University, Changchun 130061, China

Corresponding AurhorⓁ: Yin, J. Z., PhD, Professor, geosciences, mineral exploration and mining; Email address: jzyin7@jlu.edu.cn

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1. Introduction

As a rare carbon group element with distinct non-metallic properties, the silvery-gray metal germanium (Ge) exhibits excellent semiconductor characteristics. This physical and chemical property gives it a crucial position and wide application in modern technology (Hu et al., 2000; Zhang et al., 2017; Geological Museum, 2025; Guanyan, 2025). In 2018, Ge was listed as one of the 35 critical minerals by relevant U.S. authorities. Although Ge is widely distributed in the Earth's crust, it is extremely dispersed, leading to a scarcity of Ge deposits. The mining and extraction of Ge are quite challenging and therefore difficult to obtain. Its scarcity and unique physical and chemical properties make Ge an indispensable strategic mineral resource or critical metal in high-tech industries and future energy development.

The strategic value of Ge lies in its irreplaceable and widespread application in several key technological fields. Ge is used in various fields, including semiconductor devices in high-tech industries, high-precision infrared optical components in aerospace measurement and control, fiber optic amplifier materials in fiber optic communication, and infrared optical equipment in defense and military industries such as night vision devices, infrared thermal imagers, high-precision military lenses, infrared radar, radiation detectors, and nuclear reaction spectrometers. Ge is also a key material in solar cells. It is also a chemical catalyst with important applications in the biomedical field (Hu et al., 2000; Zhang et al., 2002; Yuan et al., 2011; Geological Museum, 2025; Guanyan, 2025).

Ge is iron-, sulfur-, lithophilic, and organic-friendly. In nature, it mainly exists in dispersed compound forms in sphalerite, enargite, silver, lead, and iron ores (Hu et al., 2000; Yuan et al., 2011; Zhang et al., 2017). Currently, Ge is mainly recovered as a by-product during the processing of sulfide ores such as lead, zinc, copper, silver, gold, and iron, and/or through comprehensive recovery and utilization from fly ash after coal combustion. Almost all coal in nature contains Ge, but only a very small number form Ge deposits; most coals contain very little Ge (Ao et al., 2007; Yuan et al., 2011; Yuan et al., 2012; Zhang et al., 2017).

Lead-zinc ores with a Ge content greater than 0.001% and coal with a Ge content greater than 0.002% can be mined as Ge deposits. Global Ge resources are relatively scarce. As of 2010, the global basic reserves of Ge metal were approximately 8,600 tons (Wang, 2011; Zhang et al., 2017; Geological Museum, 2025; Guanyan, 2025). These reserves are mainly distributed in the United States (3,870 tons, accounting for 45% of the global total), China (3,526 tons, accounting for 41% of the global total), and Russia (860 tons), with the remainder distributed in countries such as Germany, Belgium, and Canada. China is the world's largest producer and exporter of Ge, supplying approximately 71% of the world's Ge consumption.

Global Ge production is highly concentrated in China, the United States, and Russia, whose combined output accounts for 75% of global production. In 2022, China's Ge production reached 151 tons, of which 130 tons were primary Ge, accounting for 86.09%. Secondary recycled Ge production was 21 tons, accounting for 13.91%. In 2023, global Ge metal

production was 138 tons, of which China produced 94 tons. Since 2004, China has been the world's largest Ge producer, playing a pivotal role in the global Ge market (Wang, 2011; Geological Museum, 2025; Guanyan, 2025). China possesses abundant Ge resources, a complete Ge industry chain, and leading smelting and separation technologies, giving it a significant competitive advantage in the global Ge market. However, China remains at the lower end of the Ge industry in terms of manufacturing and application: its production mainly focuses on the rough processing of Ge ingots and products, with development and utilization limited to primary products like Ge tetrachloride and Ge dioxide. Refining and deep processing are relatively low, and most products are exported (Zhao et al., 2019). China's output of primary Ge products accounts for more than 50% of the world's total.

While China's total Ge resources are relatively abundant, high-quality resources are scarce. China's Ge resources, especially its high-grade Ge-rich coal mines, are among the few high-quality resources in the world, with Ge often occurring alongside gallium in coal. However, due to the limited mining of the main mineral, the recovery rate of Ge is not high. The comprehensive utilization level of Ge associated with lead-zinc ores, except for a few individual deposits, is generally low.

Since China implemented an export licensing program for Ge and related mineral products on August 1, 2023 (Geological Museum, 2025; Guanyan, 2025), China's Ge exports have gradually declined over the past two years. In 2023, China's cumulative exports of Ge oxide and zirconium dioxide were 15,401 tons. Since 2024, due to shortages of lead and zinc smelting raw materials and China's export controls on Ge, the global Ge industry has experienced a persistently tight supply. Coupled with increased demand for Ge used in military infrared applications, satellite solar cells, drones, photovoltaics, and optical fibers, global Ge prices have nearly doubled since the beginning of the year. As of December 20, 2024, the price of Ge ingots closed at RMB 17,750/kg (around USD $2,631/kg), an increase of RMB 8,350 (around USD $1,238) from the beginning of the year; the price of Ge dioxide closed at RMB 12,250/kg (around USD 1,816/kg), an increase of RMB 6,000 (around USD $850) from the beginning of the year.

With the development of emerging industries and the increasing demands for military informatization, global demand for Ge will continue to grow. In the infrared and fiber optic fields, Ge applications will become more widespread. The widespread application of 5G communication technology will generate substantial demand for Ge used in fiber optics. The development of emerging industries such as autonomous driving and the Internet of Things will also drive demand growth for Ge. With the intensification of geopolitical competition among major powers and the higher requirements for national defense informatization, the demand and consumption of military infrared Ge for night vision devices, detectors, infrared thermal imagers, and radar will increase significantly. Demand for Ge in fields such as biomedicine and chemical catalysts will also continue to grow (Geological Museum, 2025; Guanyan, 2025). Countries and organizations such as the United States, the European Union, Canada, Australia, and Japan have all included Ge in their critical mineral lists for strict control.

China's export controls on Ge include an export licensing system. All export activities involving Ge, including raw materials, finished products, and products containing Ge, require prior export licenses from relevant departments. After obtaining an export license,

exporting entities must comply with specific restrictions on the quantity, price, and destination of Ge exports. Relevant departments will monitor export activities throughout the entire process to ensure compliance with national requirements. For exports without a license, exports exceeding the scope of the license, or other illegal activities, China will impose administrative penalties and even pursue criminal liability according to law (Geological Museum, 2025; Guanyan, 2025).

With technological advancements and the rise of emerging industries, the demand for Ge in fields such as semiconductors, fiber optic communications, and solar cells will continue to grow. It is believed that with the continued growth of global demand over time, the Ge industry will usher in a broader prospect. With increasing environmental awareness and advancements in related recycling technologies, the recycling rate of Ge will continue to improve, thereby reducing the mining of new Ge resources, reducing environmental pollution, and achieving sustainable resource utilization.

Given the important role of Ge and the significant proportion of Ge resources in China's global reserves, this paper, based on the collection, collation, and analysis of relevant research data on Ge deposits in mainland China, classifies their industrial and genetic types and summarizes their geological and geochemical characteristics.

2. Resource overview

Ge, a dispersed element, is a silvery-gray, brittle metal with an abundance of only 0.0007% in the Earth's crust (Hu et al., 2000; Geological Museum, 2025; Guanyan, 2025). China, possessing 41% of the world's Ge resources, supplies 71% of the world's Ge products. China's Ge resources are widely distributed (Figure 1), but are mainly concentrated in 14 provinces (autonomous regions), including Yunnan, Inner Mongolia, Jilin, Guizhou, and Gansu (Figure 2) (Zhao et al., 2019; Hu et al., 2000; Guanyan, Geological Museum, 2025; Guanyan, 2025). Inner Mongolia has the richest Ge resources, accounting for 46% of China's total reserves, while Yunnan accounts for 34%. However, the Ge grade in some of these areas is low, with poor exploitability, and some are even not economically viable under current economic and technological conditions.

Of the Ge deposits with proven resources in mainland China, there are 7 deposits associated with coal mines (Figure 3), accounting for 42% of the country's proven resources; at least 16 Ge deposits associated with lead-zinc mines, accounting for 29% of the country's proven resources; at least 1 Ge deposit associated with bauxite, accounting for 12.2% of the country's proven resources; 1 Ge deposit associated with iron ore, accounting for 3% of the country's proven resources; and 5 Ge deposits associated with copper deposits, accounting for 4% of the country's proven resource. There is also 1 Ge deposit associated with uranium and coal in coal mines (i.e., the Dazhai U-Ge deposit), accounting for 7% of the country's proven resources 2% (Hu et al., 1996; Wang et al., 1999; Hu et al., 2000; Qi et al., 2002a and 2002b; Wang et al., 2003; Zhang et al., 2003; Liu, 2005; Ao et al., 2007; Zhu et al., 2009; Wang et al., 2010; Yuan et al., 2011; Yuan et al., 2012; Zhang et al., 2012; Zhou et al., 2013; Han et al., 2014; Wang et al., 2016; Zhang et al., 2017; Liu et al., 2018; Zhao et al., 2019; Liu et al., 2023).

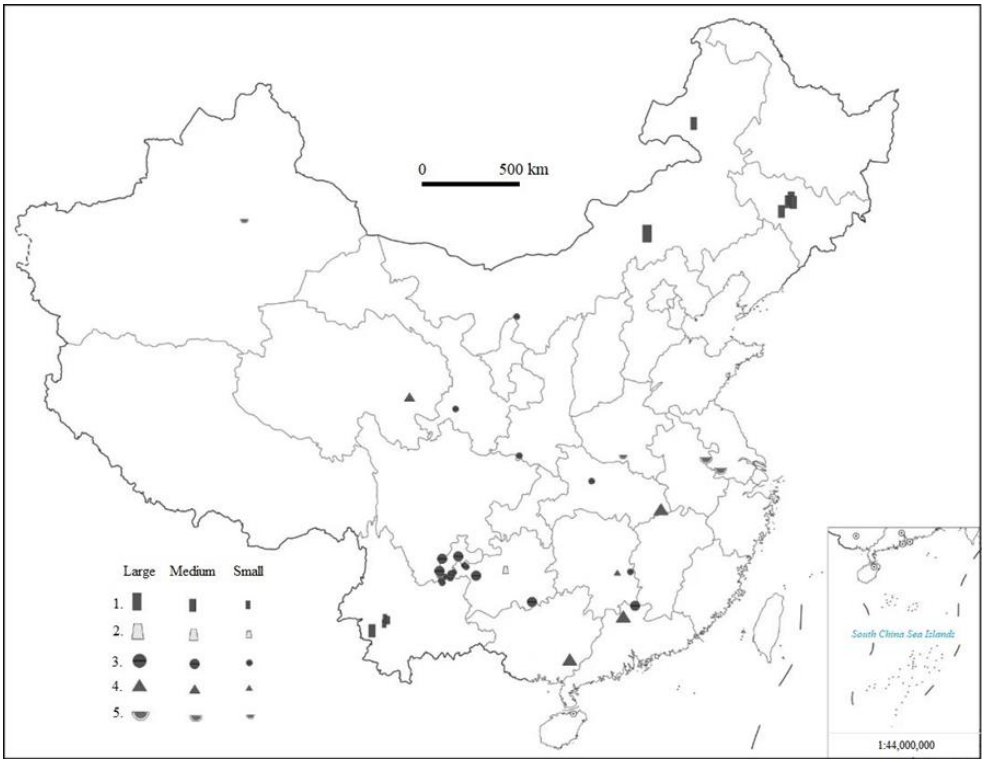


Figure 1. The known Ge deposits in mainland China (modified from Liu et al., 2023)

1. Exogenous/aqueous organic category including coal-Ge, oil shale and shale types; 2. Exogenous/aqueous inorganic category including volcano-sedimentary type, etc.; 3. Endogenous/igneous category including part of the mesothermal-epithermal types; 4. Endogenous/igneous category including hydrothermal/mesothermal-epithermal, porphyry, skarn, and part of the volcanic types; 5. Endogenous/igneous category including volcanic type

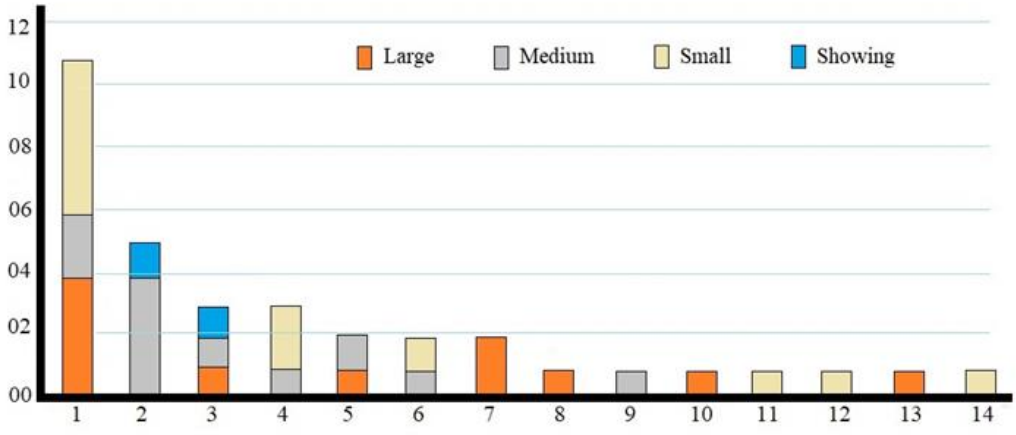


Figure 2. The number of known Ge deposits (showings) in various provinces and/or autonomous regions of mainland China (modified from Zhao et al., 2019)

1-Yunan; 2-Jilin; 3-Guizhou; 4-Gansu; 5-Sichuan; 6-Jiangsu; 7-Guangxi; 8-Shaanxi; 9-Qignhai; 10-Inner Mongolia; 11-Hubei; 12-Henan; 13-Guangdong; 14-Fujian



Figure 3. Coal-Ge deposits (showings) in mainland China (modified from Zhao et al., 2019)

China conducted a comprehensive survey of Ge resources in coal mines from the late 1950s to the early 1960s, discovering a series of Ge-bearing coal mines, mainly lignite. However, the Ge content in most coal mines in this major coal-producing country is low, making them unsuitable for industrial mining. Two Ge-bearing coal mines with independent mining value have been identified: the Bangmai Ge-bearing coal mine in the Lincang Neogene Basin of Yunnan Province and the Wulantuga Ge-bearing coal mine in the Mesozoic Basin of Inner Mongolia (Qi et al., 2002a; Ao et al., 2007; Zhu et al., 2009; Wang et al., 2016; Zhao et al., 2019).

Currently, China has four Ge mineral production bases in Yunnan, Inner Mongolia, Guangdong, and Jiangsu provinces. In 2014, China's Ge production was approximately 111.07 tons, an increase of 50 tons compared to 2005 (Wang, 2011). From 2005 to 2014, production increased approximately every three years. Production exceeded 100 tons for the first time in 2013. In 2011, China's Ge consumption surpassed Japan's, becoming the world's second-largest consumer. Ge consumption reached 32 tons in 2014, a 16.9-fold increase compared to 1.79 tons in 1987. Ge products produced in China include Ge tetrachloride, Ge oxide, Ge ingots, Ge single crystals, and organic Ge. In 2014, China's Ge consumption structure was as follows: infrared optics accounted for 69%, optical fibers for 19%, electronics and solar power generation for 6.3%, and others for 6.3%. Infrared optics is the main sector for Ge consumption in China.

Yunnan Province, located in the southwestern border region, is China's largest producer of Ge. Lincang City, relying on its lignite resources, is striving to build itself into the "Ge

Capital of Southern China," with Yunnan Lincang Xinyuan Ge Industry Co., Ltd. as its leading Ge enterprise. In addition, Chihong Zinc & Ge Co., Ltd.'s Huize Smelter processes Ge concentrate from the Huize lead-zinc mine. The joint venture, Yunnan Northern Chihong Optoelectronics Co., Ltd., produces high-purity Ge dioxide, zone-refined Ge, and downstream products. Some of Yunnan's Ge products are exported to Jiangsu, Sichuan, Hunan, and Wuhan. In 2014, Yunnan's local Ge production reached tens of tons.

Inner Mongolia, possessing China's largest Ge resources, is mainly supplied by State Grid. The group's subsidiary, Xilingol League Wulan Tuga Coal Co., Ltd., is responsible for mining. Its subsidiaries, Xilingol Tongli Ge Industry Co., Ltd. and Xilingol Mengdong Ge Industry Technology Co., Ltd., extract Ge from the flue gas after coal-fired power generation. Tongli Ge Industry, operating at full capacity, can produce tens of tons of Ge metal. Mengdong Ge Industry's capacity is approximately twice that of Tongli Ge Industry, and it also has downstream products. Ge mining in Inner Mongolia, China, is relatively concentrated, with stable output, and is increasing with the growth of Tongli Ge Industry and Mengdong Ge Industry. In addition, a certain amount of Ge is also produced in Guangdong, Jiangsu, Sichuan, Hunan, Hubei and Hebei provinces in China.

3. Spatiotemporal distribution

Known Ge deposits in mainland China are concentrated in the Sichuan-Yunnan-Guizhou Ge metallogenic belt, the Lincang coal-type Ge metallogenic belt in western Yunnan, the Xilingol coal-type Ge metallogenic belt in Inner Mongolia, and the Hami coal-type Ge metallogenic belt in Xinjiang (Figures 1-3). Among them, the average Ge content in the Ge-rich coal seams of the Naomohu coalfield in the Hami coal-type Ge metallogenic belt reaches 202×10^{-6}. The Hulunbuir coal-type Ge deposit in Inner Mongolia is located in the Yimin coalfield of the Hailar Basin. The Ge anomaly is mainly developed in interbedded rock, and the Ge resource is estimated to exceed 4,000 t. The Ge content of the main coal seams is generally between 50×10^{-6} and 200×10^{-6} (Wang, 1999). The average Ge content in the Shengli Coalfield of Inner Mongolia reaches 244×10^{-6}, and in the Baiyinwula Coalfield of Sunite Left Banner, it reaches 290×10^{-6}. Ge can be recovered from the coal ash after coal combustion at pithead power plants (Wang, 1999; Zhao et al., 2019). In the Ordos Basin coalfield, the average Ge content in the Xiaotagou Coalfield reaches 613×10^{-6}, in the Changtan Coalfield 327×10^{-6}, and in the Kongduigou Coalfield 301×10^{-6}.

The Sichuan-Yunnan-Guizhou Ge metallogenic belt contains numerous lead-zinc deposits, along with associated/symbiotic large amounts of rare metals such as Ga, Ge, and Cd, making it one of China's important rare metals producing areas. Currently, most Ge recovery in mainland China comes from Ge-rich sphalerite, with a recovery rate of around 60%. These deposits include the Daliangzi and Tianbaoshan lead-zinc mines in Sichuan, the Huize and Fule lead-zinc mines in Yunnan, and the Shanshulin, Niujiaotang, and Qingshan lead-zinc mines in Guizhou. All of these lead-zinc ores contain the dispersed element Ge (Wang et al., 2010; Zhang et al., 2012; Zhao et al., 2019).

Ge in the Lincang coal-type Ge metallogenic belt of western Yunnan is found in the Bangmai lignite-bearing clastic basin, which is based on Indosinian granite. It includes two

deposits, Dazhai and Zhongzhai, both with independent development value (Qi et al., 2002a and 2002b).

The Fankou lead-zinc deposit is a typical sedimentary-reformed Ge deposit in the northern Guangdong Ge metallogenic belt (some argue it is of hydrothermal origin), with a Ge resource of approximately 1,000 tons. Ge mainly occurs in sphalerite through isomorphous substitution with zinc (Wang et al., 2003; Chen et al., 2014).

Most known Ge mineralization in coal-bearing areas of mainland China occurred during the shrinking stages of rift basins or depressions, with favorable sedimentary environments including peat bogs and swampy lakeshores. For example, the coal-bearing strata of the Yimin coalfield are the Damoguaihe Formation and the Yimin Formation, products of the shrinking stage of the Hailar Basin, with the sedimentary environment gradually shifting from shallow lacustrine islands and lakeshores to shallow lake-swampy environments. The coal-bearing strata of the Shengli coalfield are the Lower Cretaceous Tengger Formation and the Saihantala Formation, corresponding to the uplift and shrinkage stage of the Erlian Basin in the Late Cretaceous, with the main sedimentary environment being swampy lakes.

Ge mineralization in the Sichuan-Yunnan-Guizhou metallogenic belt is controlled by tectonic and stratigraphic factors. The discovered deposits have numerous ore-bearing strata, ranging from the Neoproterozoic to the Paleozoic, with dolostone as the dominant lithology. The main ore bodies are layered, quasi-layered, vein-like, pocket-like, and/or lenticular. Ge mineralization associated with igneous activity includes porphyry, skarn, and epithermal deposits. The discovered deposits are mostly located at plate boundaries in areas of frequent tectonic and magmatic activities. The left-lateral strike-slip fault zone of the Lancang River constrained the formation and evolution of the Lincang-Bangmai Basin, hydrothermal activity within the basin, and the enrichment, mineralization, and spatial distribution of Ge (Wang et al., 2001). The mineralization epoch is concentrated in the Late Triassic to Late Cretaceous.

Ge mineralization in mainland China occurred from the Proterozoic to the Cenozoic, but was concentrated between the Mesozoic and Cenozoic. The Yanshanian period was the most developed, followed by the Himalayan and Indosinian periods. Large-scale associated/symbiotic Ge mineralization mainly developed during the Yanshanian and Himalayan periods. Ge mineralization associated with lead-zinc deposits mainly developed during the Yanshanian period, followed by the Indosinian period. Coal-type Ge mineralization mainly developed during the Jurassic and Cretaceous periods, with some development in the Late Tertiary (Wang et al., 2014; Zhao et al., 2019), but was relatively concentrated in the Mesozoic.

The formation of coal-type Ge deposits is complex, and the exact timing is difficult to determine. However, most researchers believe that Ge entered coal-bearing basins around the same time as coal formation, namely, concentrated in the Cretaceous and Neogene periods (Liu et al., 2023). Specifically, coal-type Ge deposits in the Hailar, Songliao, and Erlian basins of Northeast China formed during the Cretaceous, while the Lincang coal-type Ge deposits in Yunnan Province formed during the Neogene.

Ge mineralization in carbonate rocks is characterized by multiple phases and stages. The formation age of the ore-bearing strata covers a broad period from the Sinian to the Late Permian. However, isotopic geochronological results show that the majority of deposits were formed in the Late Paleozoic to Early Middle Paleozoic (Liu et al., 2023). For example, the ^{40}Ar-^{39}Ar age of sphalerite fluid inclusions in the Fanxian lead-zinc deposit is

(265.8±1) Ma; the Rb-Sr age of sphalerite in the Huize lead-zinc deposit is (226±6.4)～(223.5±3.9) Ma; the Rb-Sr age of sphalerite in the Qiping lead-zinc deposit is (321.7±5.8) Ma; and the Rb-Sr and Sm-Nd ages of sphalerite in the Maozu lead-zinc deposit are (190.5±5.0) Ma and (196±13) Ma, respectively. Wu et al. (2019) believe that there were two major mineralization events in the Sichuan-Yunnan-Guizhou region, at 382–328 Ma and 245–205 Ma. Among them, the mineralization events of the Middle to Late Triassic were of greater scale.

Ge mineralization related to igneous activity mainly occurred in the Late-Middle Miocene, such as the Chengmenshan copper polymetallic deposit in Jiangxi Province, where the intrusive body age is 139.1–144.5 Ma, and the Re-Os age of molybdenite in the ore body is (140±2) Ma. The diagenetic age of the Youmapo tungsten-molybdenum deposit is 109.7–100.7 Ma. The Re-Os isotopic isochron age of molybdenite in the ore body is (100.1±3.3) Ma. The Sm-Nd age of garnet in the Tongyugou copper polymetallic deposit is 216.3±1.5 Ma. Marine volcanic Ge deposits mainly formed in the Proterozoic and Early Paleozoic. However, the known number of such deposits is relatively small, and precise mineralization age data are lacking. Only the ages of the host rocks for some deposits can be collected, such as the smallest detrital zircon age of the ore-bearing strata of the Liushan Formation in the Dongchuan volcanic copper deposit in Yunnan, which is 1,220 Ma. The ore-bearing strata of the Liushanyan copper-zinc deposit are the Liushan Formation of the Erlangping Group, in which the age of the spilite porphyry is 517±84 Ma.

From the perspective of the spatiotemporal evolution of Ge mineralization in mainland China, the Huize Pb-Zn-Ge deposit is the most representative in the Sichuan-Yunnan-Guizhou Ge metallogenic belt. The mineralization occurred during the Indosinian-Yanshanian period, mainly in the late Indosinian period, with some extending into the early Yanshanian period (Han et al., 2014). The mineralization age of the Fankou Pb-Zn-Ge deposit in the northern Guangdong Ge metallogenic belt is approximately in the late Early Cretaceous, with a relatively long duration (Zhu et al., 2013). Similar in genesis to the Fankou Pb-Zn-Ge deposit, the Beishan Pb-Zn-Ge deposit in Guangxi was formed from mineralized hot brine produced during the formation of the Devonian-Permian basin due to compaction and dehydration. This hot brine migrated to favorable locations during the Yanshanian period and precipitated to form minerals (Liu et al., 2018). Coal-type Ge mineralization is relatively young. The Xilingol coal-type Ge metallogenic belt in Inner Mongolia is Cretaceous, the Hami coal-type Ge metallogenic belt in Xinjiang is Jurassic, the Lincang coal-type Ge metallogenic belt in western Yunnan is mainly Neogene, and the Hulunbuir coal-type Ge metallogenic belt is mainly Late Jurassic and Early Cretaceous.

Ge mineralization is commonly found in lead, zinc, silver, copper, and molybdenum sulfides and in coal seams. In lead-zinc ores, Ge typically exists as an isomorphism within the zinc sphalerite lattice. Under strong reducing and low-temperature conditions, Ge^{4+} transforms into Ge^{2+}, with an ionic radius similar to Zn^{2+}, making it easier to enter the zinc sphalerite lattice (Liu, 2005). The Ge grade in coal seams varies considerably, primarily concentrated at the top and/or bottom. The Ge in the coal seams of the Lincang Bangmai Basin in Yunnan Province likely originates primarily from surrounding metamorphic rocks, granites, and the basin's basement strata (Zhu, 2009). However, Hu et al., based on the spatial distribution patterns of coal-type Ge mineralization and siliceous rocks, the sulfur isotope composition of pyrite, the grade variation patterns of Ge in coal seams, and the geochemical characteristics of siliceous rocks (Hu et al., 1996 and 2000), believe that Ge

mainly originates from hydrothermal solutions, and that the Ge in these solutions is primarily supplied by the Ge-rich granites at the basin's basement (Zhang et al., 2003).
Overall, about half of China's proven Ge resources are associated with coal mines, while the majority of the remainder is associated with non-ferrous metal minerals such as lead-zinc deposits. Ge can be found in various deposits from different eras, including endogenic hydrothermal polymetallic deposits, Ge-bearing organic rock deposits, and sedimentary reformed deposits, with the first two being the most prevalent, accounting for 64% of all Ge resources. China's high-grade coal-type Ge is a rare and high-quality resource in the world.

4. Type and characteristics

Some Chinese scholars have classified associated/symbiotic Ge deposits in the country into three main types (Wang, 2011): mesothermal-epithermal polymetallic associated/symbiotic Ge deposits, Ge-bearing organic rock deposits, and sedimentary reformed Ge deposits. They concluded that Ge mineralization in mainland China is mainly composed of mesothermal-epithermal deposits and Ge-bearing organic rock deposits, accounting for 64% of all Ge deposit types. Other Chinese researchers have further elaborated (Ao et al., 2007) that mesothermal-epithermal polymetallic deposits are the most common type of associated/symbiotic Ge deposit, with typical examples including the Kuangshanchang, Qilinchang, and Yulu lead-zinc deposits in Yunnan. Ge-bearing organic rock deposits refer to deposits where Ge is co-occurring and/or associated with coal, oil shale, and black shale. The Bangmai Ge deposit in Lincang, Yunnan, is a rare, independently mineable Ge deposit within coal-bearing strata in mainland China and even the world (Zhu, 2009), with large-scale reserves. The Wulantuga coal-type Ge deposit in the Shengli coalfield of Inner Mongolia has resources approaching 3,000 tons. Sedimentary reformed type Ge deposits, such as the Maomaochang-Zhazichang lead-zinc deposit in Guizhou, have Ge content in zinc oxide reaching 390 g/t. Hydrothermal replacement Ge mineralization is generally small in scale, such as the Shizhuang lead-zinc deposit in Yunnan and the Luoyang iron deposit in Fujian (Yuan et al., 2011 and 2012; Zhou et al., 2013; Zhang et al., 2014).
Some other researchers classify Ge deposits in mainland China into coal-bearing Ge deposits occurring in coal-bearing sediments, such as the Wulantuga coal-Ge deposit in Shengli Coalfield, the Wumuchang coal-Ge deposit in Yimin Coalfield, the Dazhai coal-Ge deposit in Lincang, and the Yingcheng coal-Ge deposit. Carbonate rock-hosted Ge deposits are the most numerous and have the most mature recovery and utilization technologies. These include porphyry, skarn, and epithermal deposits, which are magmatic-hydrothermal Ge-rich deposits related to magmatic-hydrothermal activity. This includes volcanic-type Ge deposits, encompassing both marine and terrestrial volcanic rock deposits, as well as other sedimentary Ge deposits besides coal-bearing Ge deposits, such as associated Ge in bauxite and phosphate deposits.
Clearly, these classifications are rather rough. Some types have no connection to their “origin” or their genesis is unclear. They also lack in-depth research and analysis of known Ge deposits in the country, hindering overseas researchers from understanding their true nature.
Based on a detailed review of existing research literature on Ge deposits in mainland China, this paper classifies currently known associated/symbiotic Ge deposits in the country into

three main categories: endogenous, exogenous, and a mixture of both (Table 1). The former are closely related to igneous activity and can be further subdivided into mesothermal-epithermal, skarn, porphyry, volcanic, and volcanic sedimentary types. The exogenous types are closely related to sedimentary and hydrothermal activity and can be further subdivided into organic coal deposits, inorganic bauxite deposits, and phosphate deposits. At the same time, it was predicted that mainland China might become the first in the world to discover independent Ge deposits in and around the Qinghai-Tibet Plateau. These are briefly described below.

Table 1. Type and representative Ge deposit in mainland China

Type					Representative deposit	Data source
Industrial	Genetic			MA[1]		
Symbiotic/Associated	Endogenous	Igneous	M-E[2]	Pb-Zn-Ge	Luoba in Gansu, Huidong in Sichuan, and Huize in Yunnan, etc.	Gao, 1963
				Pb-Zn-Ag-Ge	Huidong in Sichuan, and Yingde in Guangdong, etc.	Luo et al., 1963
				Cu-Sn-Ge	Qinjia in Guangxi, etc.	Wang, 1988
				Cu-Zn-Ge	Liushanyan (Dahe) in Henan, etc.	Lu et al., 2000
				Cu-Ge	Xiaohankou in Hubei, etc.	Qi, 2002
				Ag-Pb-Ge	Xialadi in Gansu, etc.	Xue et al., 2006
				Zn-Ge	Nanmushu in Shaanxi, and Woqianchang in Yunnan, etc.	Wang et al., 2015
				Pb-Zn-P-Ge	Huize in Yunnan, etc.	Lin et al., 2016
				Pb-Zn-S-Ge	Beishan in Guangxi, etc.	Wang et al., 2016
				Wu-Mo-Ge	Youmapo in Guangxi (Ge reserves: 319 tons), etc.	Huang et al., 2018
				Cu-Ge polymetallic	Jiujiang in Jiangxi, etc.	Zhao et al., 2019
			Volcanic	Cu-Fe-Ge	Lanniping & Shijiangjun in Yunnan, Tongyugou in Qinghai, etc.	Weng et al., 2020
				Cu-Zn-Ge	Dahe, Tongbai in Henan, etc.	Duan et al., 2022
				Ag-Pb-Ge	Xialadi in Gansu, etc.	Liu et al., 2023
				W-Cu-S-Ge	Caihuagou in Xinjiang, etc.	Xue et al., 2024
				Cu-Ge polymetallic	The Volcanic basin in Lishui, Jiangsu etc.	Gegological Museum, 2025
				Fe-Mn-Ge	The Volcanic basin in Lishui, Jiangsu etc.	Guanyan, 2025
				Fe-Ge	The Volcanic basin in Lishui, Jiangsu etc.	Huang et al., 2026
			Skarn	Cu-S-Ge	Jiujiang in Jiangxi, etc.	Liu et al., 2026
				S-Ge	Shangpu, Laiyang in Shandong, etc.	You et al., 2026;
				Fe-Ge-Ga	Fujian, etc.	
			Porphyry	Cu-Ge polymetallic	Late Yanshan quartz porphyry in Jiangxi, etc.	
	E&XH[3]	I&A[4]	VS[5]	Fe-Ge-U	The Volcanic basin in Lishui, Jiangsu etc.	
	Exogenous	Aqueous	Organic	Coal-Ge	Inner Mongolia's Ulantuga, Yunnan's Dazhai & Bangmai, etc.	
				Oil shale	No related mineral deposit has been developed yet	
				Shale	No related mineral deposit has been developed yet	
			Inorganic	P-Ge	Huize in Yunnan, etc.	
				Bauxite-Ga-Ge	Xiaoshanba in Guizhou, etc.	
				Pb-Zn -Ge	Kuangshanchang in Yunnan, etc.	
Independent			No findings yet, but the future looks promising.			

Note: MA[1] - Mineralization assemblage; M-E[2] - mesothermal-epithermal; E&XH[3] - Endogenous and exogenous hybrid; I&A[4] - Igneous and Aqueous hybrid; VS[5] - volcano-sedimentary.

4.1 Endogenous igneous

The endogenous igneous associated/symbiotic Ge deposits discovered in mainland China mainly include the following genetic types.

4.1.1 Mesothermal-epithermal

This type of Ge deposit includes what previous researchers called carbonate rock hosted types. Classifying genetic types based on the host rock is clearly inappropriate. Practice has shown that mineralization of different genetic types in the same region can occur entirely within the same host rock. In fact, these Ge mineralization hosted in carbonate rocks are genetically closely related to hydrothermal fluids generated by magmatic activity, and should be classified as magmatic mesothermal-epithermal deposits. Based on currently published data, this type of Ge mineralization is the most numerous in mainland China, and its recovery and utilization technology is relatively mature. Mesothermal-epithermal Ge deposits are mainly distributed in the Sichuan-Yunnan-Guizhou metallogenic belt and the Nanling metallogenic belt. The Sichuan-Yunnan-Guizhou region is the area with the densest distribution of this type of Ge deposit, with representative deposits such as several large and medium-sized Ge deposits in Huize and Qiping. The host rock alteration of this type of deposit is generally weak, with the main alterations including calcitization and dolomitization, followed by ankeritization and silicification. Based on their main mineral composition, these deposits can be further subdivided into numerous subcategories, such as Pb-Zn-Ge, Pb-Zn-Ag-Ge, Cu-Sn-Ge, Cu-Zn-Ge, and Ag-Pb-Ge (Table 1). The primary minerals in mesothermal-epithermal Ge mineralization are mainly sphalerite, galena, and pyrite, with minor amounts of chalcopyrite, stibarsen, and dufrenoysite. Secondary minerals include smithsonite, cerussite, anglesite, limonite, and hemimorphite. The minerals are mainly found in massive, banded, vein-like, disseminated, and fine veinlet forms. Ge is primarily found in sphalerite and smithsonite. Vein minerals are mainly dolomite and calcite, with some deposits containing quartz, barite, fluorite, sericite, gorse, carbonaceous minerals, and asphalt.

While some deposits contain high levels of Ge, sphalerite formed at low temperatures remains the primary carrier of hydrothermal Ge mineralization. Direct substitution and/or coupled substitution between elements are likely the main mode of Ge entry into sphalerite. Studies have shown a good correlation between Ge and copper content in sphalerite; Ge^{4+} and Cu^{2+} can isomorphously substitute Zn^{2+} in the sphalerite lattice through coupling, and combinations of In^{3+} and Ge^{4+} can also substitute Zn^{2+}. The phenomenon of Ge^{4+} substituting for Zn^{2+} and/or Ge^{2+} substituting for Zn^{2+} has been observed in the Uss River Pb-Zn-Ge deposit.

Ge in hydrothermal Ge deposits may originate from the basement and/or ferruginous rocks in adjacent areas. In the Sichuan-Yunnan-Guizhou region, Ge abundance in both the basement and cap-rock is lower than in the crust, but the Ge background value in the basement is higher than in the cap-rock. Sedimentary Ge-rich phosphate deposits and ferruginous Ge mineralization are developed near the basement strata, such as the Dajing lead-zinc-phosphate deposit and the Lanniping Cu-Ge deposit. In some regional deposits, such as the Fule and Qiping lead-zinc deposits, the sulfide lead isotope characteristics are similar to those of the Kunyang Group in the basement, indicating that the basement is a source of ore-forming materials for some deposits. Although the Ge background value in the Emeishan Wuluite and Xuanwei Formation is lower than that in the basement, it is higher than that in the adjacent upper and lower strata, suggesting a potential to provide certain ore-forming materials.

The fluids found in Ge-rich deposits in China are characterized by low temperature (100–150 °C) and moderate salinity (w(NaCleq) = 10%–30%). The fluids mainly originate from basin brines, but some deposits exhibit characteristics of deep crustal fluids. Generally, the Ge content in lead-zinc deposits gradually increases as the fluid temperature decreases. However, when multiple generations of sphalerite exist, the Ge content in early-generation sphalerite is not necessarily lower than that in later-generation sphalerite due to factors such as the residual Ge content in the fluid, the content of ore-forming coupling/competing elements, temperature, and pH. For example, in the Huize lead-zinc deposit, three generations of sphalerite (Sp1, Sp2, and Sp3) develop from high to low temperature, but the Ge content, from high to low, is Sp3 > Sp1 > Sp2. In the Wusihe Ge-rich lead-zinc deposit, the Ge content in the Sp1 sphalerite, which formed at a higher temperature, is higher than that in the Sp2 sphalerite, which formed at a lower temperature. Meng (2026), through his study of sphalerite in two typical Ge-rich lead-zinc deposits in the Sichuan-Yunnan-Guizhou metallogenic region of China—the Huize deposit in Yunnan and the Wusihe deposit in Sichuan—concluded that the sphalerite in the Huize deposit is divided into three phases: early dark brown (Sp1), middle yellowish-brown (Sp2), and late reddish-brown (Sp3). The sphalerite in the Wusihe deposit has two phases: sedimentary (Sp1) and hydrothermal (Sp2). The mineral assemblage of the Huize deposit is relatively simple: the ore minerals are mainly pyrite, sphalerite, galena, and jamesonite, while the gangue minerals are mainly calcite, dolomite, and clay minerals. The ore minerals of the Wusihe deposit are mainly pyrite, sphalerite, galena, and jamesonite, while the gangue minerals are mainly dolomite, quartz, apatite, rutile, and pitch. The sphalerite in the Huize lead-zinc deposit has a relatively simple structure and is relatively clean internally, with no exsolution minerals or independent Ge minerals present. It is inferred that Ge mainly exists as isomorphous minerals within the sphalerite. The sphalerite in the Wusihe lead-zinc deposit has a more complex structure, with pyrite visible as fine thread-like inclusions within the sphalerite, and numerous internal impurities, including micron-nano-sized sulfonate minerals, galena, and germanite (GeO_2). It is inferred that Ge may exist simultaneously as independent minerals, nanoparticles, and isomorphous minerals. Scanning electron microscopy revealed abundant jordanite and geocronite within both the Huize and Wusihe lead-zinc deposits. Electron probe microanalysis showed that the average Ge content of sulfonate minerals in the Huize lead-zinc deposit was 0.05%. A new mineral, ruizhongite, was discovered in the Wusihe lead-zinc deposit. The Ge content in sphalerite within the Kuangshan and Qilin sections of the Huize lead-zinc deposit is roughly the same: late-stage reddish-brown Sp3 (average Ge 151.64 ppm) is richer in Ge than dark brown Sp1 (average Ge 32.93 ppm) and yellowish-brown Sp2 (average Ge 45.73 ppm), and there is no significant correlation between sphalerite color and Ge enrichment under transmitted light. The Ge content in sphalerite from the hydrothermal mineralization period of the Wusihe lead-zinc deposit is relatively high, ranging from 0.87 to 2,305.29 ppm, with an average of 319.34 ppm. The Wusihe lead-zinc deposit sphalerite contains a large number of independent minerals of Ge at the micron-nano scale, as well as galena and sulfide minerals. Low to medium temperature, low sulfur fugacity, weak alkalinity, and high Cu activity in the fluid are likely the main reasons for the formation of Ge-rich sphalerite in the Huize lead-zinc deposit. High Cu and Ag activities, high oxygen fugacity, high sulfur fugacity, and acid-neutral conditions in the fluid are likely the main reasons for the formation of Ge-rich sphalerite and other Ge-rich minerals in the Ussghe lead-zinc deposit. Sun et al. (2025) found that the Ussghe lead-zinc deposit, during its hydrothermal

phase, contained a stage I of darker-colored sphalerite and a stage II of lighter-colored sphalerite, with average visual reflectance values of 16.126% and 16.187%, respectively; average dominant reflectance wavelengths of 474.179 nm and 474.164 nm, respectively; average reflectance saturation values of 0.048 and 0.043, respectively; and average Ge contents of 244.33×10^6 and 43.22×10^6, respectively. Ge exists isomorphously in the sphalerite and is more readily enriched in sphalerite with high reflectance saturation. The substitution mechanism of Ge is related to Cu and Ag. The reflectance color index of Ge-rich sphalerite indicate an upper limit of mineralization temperature of 203.0-293.0 ℃, while the trace element characteristics indicate a lower limit of mineralization temperature of 83.3-199.0 ℃. The deposit is genetically classified as a Mississippi Valley-type (MVT) lead-zinc deposit.

4.1.2 Volcanic

Known volcanic-type associated/symbiotic Ge mineralization in mainland China can be classified into various mineralization assemblages based on their main mineral types, including Cu-Zn-Ge, Ag-Pb-Ge, Cu-Fe-Ge, W-Cu-S-Ge, Cu-Ge polymetallic deposits, and so on (Table 1). These discovered deposits are mostly located in areas with frequent tectonic-magmatic activity at plate boundaries, with mineralization epochs concentrated in the Late Triassic to Late Cretaceous. Representative deposits include the Liushanyan (Dahe) Cu-Zn-Ge deposit in Tongbai County, Henan Province; the Shijiangjun deposit in Dongchuan County, Yunnan Province; the Tongyugou Cu-Ge deposit in Qinghai Province; and the Cu-Ge-Sr polymetallic deposit in the Dongshantou volcanic basin in Lishui County, Jiangsu Province.

These Ge deposits can be further subdivided into marine volcanic and terrestrial volcanic. Globally, Ge deposits associated with marine volcanic activity are mainly a few Kuroko ore deposit or black ore deposits in Japan and Spain, among others. The number of such deposits discovered in mainland China is extremely small, with the main metallogenic epochs being the Paleoproterozoic and Early Paleozoic.

The known but controversial Paleoproterozoic marine volcanic Ge deposits in mainland China are primarily Ge-rich Dongchuan-type copper deposits. The ore bodies in these deposits are mainly hosted in volcanic rocks. Taking the Lanniping copper deposit as an example, the host rocks include metamorphosed tuff, diabase, gabbro, biotite-altered rocks, gray-siliceous rocks, and tuffaceous dolomite rocks in the transition zone between the Yinling Formation and the Luoxue Formation. The ore bodies include copper ore bodies and copper-iron ore bodies, mostly occurring in layered to quasi-layered formations. The main minerals are bornite, chalcopyrite, tetrahedrite, hematite, chalcocite, and magnetite. Hu (2010) reported 47 t of associated/symbiotic Ge in copper deposits, but the specific grade and occurrence state are unclear.

Early Paleozoic Ge-rich deposits in mainland China include the Liushanyan copper-zinc deposit and the Caihuagou tungsten-copper-pyrite deposit (Table 1). The ore bodies of these deposits are mainly hosted in acidic volcanic rocks. The Liushanyan copper-zinc deposit formed in a back-arc environment, with the ore-bearing strata being the Erlangping Group, belonging to the intraplate-enlarged back-arc basin submarine volcanic sedimentary metamorphic spilite porphyry (Zeng, 2012). The Caihuagou copper-sulfur polymetallic deposit occurs in marine rhyolite.

Typical galvanic-type massive sulfide deposits exhibit distinct vertical zoning. The mineral assemblage, from top to bottom, consists of a barite zone (barite content greater than sulfide), a Kuroko ore zone or a lead-zinc ore zone (rich in sphalerite), a chalcopyrite ore zone (rich in copper ore), and a pyrite ore zone. The alteration of the surrounding rocks, from the central to the periphery, consists of sericitization and chloritization zone, montmorillonitization zone, and zeolite zone. The main minerals include pyrite, sphalerite, chalcopyrite, and galena. Ge-bearing minerals include sphalerite (up to 370×10^{-6}), renierite, Ge-bearing bornite, and Ge-bearing colusite. The gangue minerals are mainly quartz, sericite, barite, gypsum, scleroderma, and chlorite.

Whether it's the Liushanyan or Caihuagou deposits, the ore bodies are all tectonically controlled to a certain extent, exhibiting complex morphologies, including banded, lenticular, or vein-like forms. The alteration and mineralization of the surrounding rocks near the ore are more intense than those further away. The intensity of alteration and mineralization in each deposit gradually decreases from top to bottom. Taking the Caihuagou sulfur-copper polymetallic deposit as an example, the top of the deposit consists of layered and quasi-layered polymetallic sulfide ore bodies formed by volcanic eruption and sedimentation, while the bottom consists of banded and veinlet pyrite bodies formed by volcanic-hydrothermal alteration. The main alterations in the Caihuagou sulfur-copper polymetallic deposit include silicification, baritization, sericitization, chloritization, and pyritization, with higher intensity baritization and pyritization near the ore bodies. The mineral structure is mainly semi-anthromorphous to anhedral granular, with massive, sparse to dense disseminated textures. Minerals include pyrite, magnetite, chalcopyrite, bornite, and sphalerite.

In China, continental volcanic/subvolcanic Ge mineralization is mainly distributed in the Lishui Volcanic Basin of Jiangsu Province, with discovered deposits including Wanshoushan, Nanshantou, and Dongshantou. These Ge deposits are associated with large-scale volcanic eruptions in the Early Cretaceous (Meng et al., 2022), and the ore-bearing formations are fluvial-lacustrine sediments occurring between two eruptive cycles. The main host rocks are iron-bearing siliceous rocks. Ore bodies occur mostly as stratiform, flattened, and irregular shapes, clearly controlled by tectonics and stratigraphy. The main mineral type is Ge-containing iron-manganese ore, followed by Ge-containing iron ore, etc.

The Wanshoushan deposit is located in the Erdingshan-Lujia'ao overturned anticline, and the ore bodies are controlled by an east-west trending fracture zone (You et al., 2026). There are a total of 35 ore bodies, one of which is a continuous, gently undulating, irregular vein-like ore body, 900 meters long, 0.59-17.10 meters thick, with an average thickness of 5.42 meters, and a depth of 105-360 meters. The remaining 34 smaller ore bodies are mostly located above and parallel to the main ore body, exhibiting vein-like or lenticular shapes, 5-64 meters long, with a maximum thickness of 4.5 meters, generally less than 1 meter. The ore minerals are mainly Ge-bearing hematite, with minor amounts of specularite, trace amounts of magnetite and limonite. The ore has a colloidal structure, exhibiting oolitic, botryoidal, crust-like, and brecciated textures. The ore contains 0.001%-0.0168% Ge, generally 0.003%, with the usable ore averaging 0.0035% Ge. Ge is found in hematite, and its grade is directly proportional to the iron content. Generally, when the iron content is greater than 5%-10%, the Ge content can reach the cut-off grade, i.e., above 0.001%; when the iron content is greater than 10%-15%, the Ge content can reach 0.002%.

The Ge mineralization in the Nanshantou-Shizishan area of the volcanic basin in Lishui County, Jiangsu Province, is closely related to the spatial relationship of the small intrusive

bodies exposed in the area, and may have a genetic relationship (You et al., 2026). The volcanic breccia in the area was likely formed by volcanic eruptions deposited in shallow water; therefore, the strata in the area are volcanic sedimentary rocks. From April 1960 to March 1963, relevant investigations found that the Ge grade in the iron ore was close to the Ge cut-off grade, basically meeting the requirements for Ge ore, thus confirming that the deposit is a Ge deposit.

4.1.3 Skarn

Studies have shown that Ge does not exhibit significant selective enrichment in different intrusive and volcanic rocks; that is, its background values are not significantly different, with slight enrichment only observed in some highly differentiated or volatile-rich rock bodies. Ge-rich rocks discovered in mainland China are typically late-stage intermediate-acidic facies within complex intrusive bodies. For example, the ore-forming rock body of the Youmapo skarn tungsten-molybdenum deposit is a late-stage muscovite granite from the Yanshan period complex intrusive body, containing accessory minerals such as fluorite, ilmenite, and sulfides, and exhibiting high silica, high fluorite content, and low oxygen fugacity. The ore-forming rock body of the Chengmenshan skarn-type copper polymetallic deposit is a late-stage quartz porphyry from a Yanshan period intermediate-acidic shallow-to-hypershallow complex intrusive body. The ore-forming intrusion of Saishitang-Tongyugou is a late-stage granodiorite from a Late Triassic complex.

Skarn-type Ge mineralization is often not isolated, but rather occurs in conjunction with porphyry and/or even mesothermal-epithermal Ge mineralization, forming a multi-genetic Ge metallogenic series. A typical example is the Chengmenshan skarn-type copper polymetallic deposit in Jiangxi Province, which is essentially a coexistence of skarn and porphyry types.

Jiang et al. (2020) reported that the Ge content of the raw ore in a skarn-type Ge-Ga-Fe deposit in Fujian Province reached 52×10^{-6} (measured by plasma mass spectrometry at the Guangdong Provincial Institute of Mineral Resources). Guo et al. (2021) reported the discovery of a small amount of copper ore samples with relatively high Ge content in carbonate metasomatic ore bodies in the Chengmenshan copper polymetallic deposit. This data was obtained using electron probe microanalysis.

4.1.4 Porphyry

Internationally, Ge-rich ore bodies genetically linked to igneous activity are mostly distributed in the marginal zones of porphyry systems, and these ore bodies are often vein-like and/or brecciated, exhibiting distinct medium-to-low temperature mineralization characteristics. Influenced by mineralization type and ore-forming element assemblages, Ge in these deposits is found in a wide variety of minerals. For example, in porphyry-hydrothermal vein-type Cu-Mo-Au deposits, Ge may be enriched in bornite, enargite, domeykite, and covellite, while in hydrothermal vein-type Ag-Pb-Zn deposits, Ge is mainly enriched in sphalerite, and so on.

Similar to other genetic types, porphyry-type Ge mineralization is not isolated but often occurs alongside skarn-type and igneous-hydrothermal Ge mineralization within the same

tectonic-magmatic-stratigraphic system. Sometimes, these endogenous and exogenous Ge mineralizations even coexist, forming a relatively complete metallogenic series.

4.2 Igneous and aqueous mixed

Igneous and aqueous mixed Ge mineralization often occurs in volcanic basins. Similar mixed endogenous and exogenous mineralizations of other minerals also frequently occur in volcanic basins. A typical example is the Nanshantou Fe-U-Ge deposit in the volcanic basin of Lishui County, Jiangsu Province, China.
Volcanic basins are often sites where igneous and aqueous activities coexist and thrive, thus providing an optimal environment for the combined occurrence of endogenous and exogenous mineralization.

4.3 Exogenous aqueous

In fact, it is a type of Ge mineralization related to sedimentation. According to its main mineral composition, it is divided into two major categories: organic and inorganic.

4.3.1 Aqueous organic

Aqueous organic Ge mineralization refers to those occuring primarily in natural fossil fuels, such as coals. Currently, the most abundant and exploited Ge resources of this type are mainly Ge deposits in coal-bearing sediments; therefore, this paper refers to them as coal type.

- **Coal type**

China's discovered coal-type Ge deposits include the Shengli Coal Mine-Wulantug Deposit, the Yimin Coal Mine-Wumanchang Deposit, and the Lincang Dazhai, Caiba, and Yingcheng Coal Mine Deposits.

Studies have shown that the spatial distribution of Ge ore bodies in different coal deposits varies due to factors such as the location of Ge-rich magmatic/volcanic rocks and the migration pathways of Ge-rich hydrothermal fluids. For example, in the Lincang coal-Ge deposit, Ge-rich sections are mainly distributed in the first coal-bearing section near the basin basement (Hu et al., 2000). In the Wulantuga coal-Ge deposit, the Ge-rich No. 6-1 coal seam is located near the western edge of the basin. The enrichment locations of Ge also differ at the coal seam scale. For instance, in the Lincang Basin, the Ge enrichment pattern conforms to Zilbermints' law, mainly distributed in the top and bottom plates of Ge-bearing coal seams; while in the Shengli Coal Mine, the Ge-rich ore body in the No. 6-1 coal seam is mainly distributed in the middle of the coal seam.

Coal-type Ge deposits are mainly composed of low-rank lignite and long-flame coal. In addition to common organic components, the ore also contains silicate minerals such as quartz, plagioclase, and illite, as well as sulfides such as ferrous ore. Ge in coal is mainly

enriched in the organic matter, but the relationship between the enrichment degree of Ge and the petrographic composition of the coal is still unclear. For example, in high-grade Ge-rich coal mines, samples from the Lincang area are dominated by humic components, with a content of 88.5%-99.5%, while the inertinite content is only 0%-8.3%. However, in the Wulantuga Ge mine samples, the humic component content is only 33.1%-69.8%, while the average inertinite content is as high as 52.5%. Among the organic components, except for trace amounts of Ge detected in some hydrothermal pyrite, most minerals do not contain Ge.

Extensive research indicates that Ge in coal-type Ge deposits mainly originates from intermediate-acidic intrusive rocks, volcanic rocks, or volcanic clastic rocks adjacent to coal-bearing basins. Among these, the Ge-rich rocks in the Lincang area consist of a stock-like set of two-mica granite, dating to the Middle to Late Triassic. The rock mass is rich in potassium and silicon but poor in iron and titanium, representing a product of magmatic fractionation and crystallization under post-collisional conditions. The rock mass contains 3.5×10^{-6} Ge, exhibiting a relatively high Ge leaching rate. However, there is limited research on Ge-rich rock masses in the Wulantuga and Yimin areas. Qin (2001) found that the w(Ge) of the western monzogranite and diorite samples from the Wulantuga coal-type Ge deposit was above 15×10^{-6}. Du et al. (2009), after conducting geochemical tests on various intrusive rocks and volcanic rocks surrounding the same deposit, found that only in the silicified Late Jurassic rhyolitic conglomerate lava was a relatively high Ge content (approximately 5×10^{-6}).

Clearly, even so-called aqueous coal-type Ge mineralization is not purely a result of sedimentary processes, but is closely related to igneous activity; that is, it is the result of the combined effects of endogenous and exogenous geological processes, with each intertwined.

The entry of Ge from its source region into the coal-bearing basin and its eventual mineralization is a complex process, influenced by various factors such as paleogeography, paleoclimate, and igneous activity. Furthermore, hydrothermal activity within the basin is also a crucial condition for the formation of Ge deposits. For example, the overall trace element variation of siliceous rock interlayers and the underlying two-mica granite in the Lincang coal mine are similar, indicating that the hydrothermal fluids that formed the siliceous rocks carried a large amount of trace elements, including Ge, from the granite. In the Wulantuga coal-type Ge deposit, Ge enrichment benefits from non-magmatic N_2-bearing alkaline hydrothermal fluids and mixed hydrothermal fluids from other sources. In the Hunchun coalfield in the eastern Yingcheng Basin, Guo et al. (2019) used SEM-EDS to find quartz and pyrite filling fractures in some Ge-rich coal samples, indicating that Ge enrichment in this deposit may also be related to hydrothermal activity.

Huang et al., through statistical analysis of Ge content data from a large number of coalfield exploration data, concluded that the average Ge content in major coalfields in Northeast China is 1-5 μg/g, which is close to the average Ge content in Chinese coal mines. In the Shengli coalfield, where the typical coal-type Ge deposit Wulantuga is located, and the Yimin coalfield, where Wumuchang is located, the average Ge content in coal is 2.63 μg/g and 3.30 μg/g, respectively, which are not significantly different from the average Ge content in Chinese coal mines. The enrichment of Ge in coal is characterized by small-scale

accumulation, with hydrothermal minerals commonly found in the enriched areas, indicating that hydrothermal intrusion provides favorable conditions for Ge enrichment in coal.

- **Oil shale**

There is currently no published research on this topic, although this type of statement exists.

- **Shale**

There is currently no published research on this topic, although this type of statement exists.

4.3.2 Aqueous inorganic

These types of Ge mineralization include bauxite, phosphate, iron, and lead-zinc placer deposits. Reported non-coal sedimentary Ge-rich deposits include the Xiaoshanba bauxite deposit and some phosphate deposits. The metallogenic geological setting and ore-bearing strata of these deposits are not strongly correlated with the degree of Ge enrichment, and the Ge in most of these deposits has not been recovered and utilized, making their development and utilization prospects unclear.

- **Bauxite type**

The Xiaoshanba bauxite deposit is located in northern Guizhou Province and is a sedimentary diaspore bauxite deposit. The ore-bearing strata are the Jiujialu Formation of the Lower Carboniferous. The main minerals are earthy bauxite, semi-earthy bauxite, gravelly oolitic bauxite, and massive bauxite. As of 2009, the cumulative Ge resource was 1,623.81 t. Ye et al. (2008) conducted ICP-MS tests on various types of bauxite ore samples in this deposit and found that the sample with the highest Ge content was earthy bauxite, but it had not yet reached the current minimum industrial grade requirements.

- **Phosphate type**

Sedimentary phosphate deposits of Ge represent another potential source of Ge. Studies indicate that approximately one-third of phosphate deposits in mainland China contain various associated metals, including Ge. Taking the Huize area as an example, the locations of phosphate deposits in the region are often close to hydrothermal Ge mineralization. Some phosphate deposits and Ge mineralizations are even integrated into the same exploration area, such as the Dashuijing lead-zinc and phosphate exploration area. Studies by Zhang et al. (2015) on Shifang-type phosphate deposits suggest that Ge and other dispersed elements may be enriched in phosphate rocks and sulfur-phosphorus-aluminum-strontium deposits. Although current research on the geochemical behavior of Ge in phosphate deposits is limited, its organic affinity allows it to accumulate to a certain extent

during phosphorogenesis under suitable environment. The main phosphorus-bearing layer in the Huize area is the Lower Cambrian Yuhucun Formation, which is also one of the potential source layers for Ge in the region. Therefore, although the exploitability of Ge in phosphate rock is still unclear, the Ge-generating potential of phosphate rock in Huize area is still worth further attention.

5. Discussion

Based on the three-tiered metallogenic belts, researchers have divided Ge deposits in mainland China into 15 Ge-forming belts according to their spatial distribution patterns (Liu et al., 2023). Coal-type Ge mineralization is distributed in the Neogene basins and Songliao Basin on the western side of the Greater Khingan Mountains, involving the Hailar Basin Ge-forming belt (Ge1), the Erlian Basin Ge-forming belt, and the Songliao Basin Ge-forming belt. Neogene coal-type Ge deposits are mainly found in the Lincang Basin Ge-forming belt.

Mesothermal-epithermal Ge mineralization is concentrated in the Sichuan-Yunnan-Guizhou region along the western margin of the Yangzi Platform, including the Upper Yangzi-Eastern Yunnan-Southern Sichuan-Guizhou metallogenic belt and the Upper Yangzi-Eastern (folded belt) metallogenic belt-Hunan-Hubei-Southern Guizhou metallogenic sub-belt. Other Ge mineralizations and Ge-rich deposits of this type are scattered along the northern margin of the Yangzi Platform and the western margin of the North China Platform, including the Ordos western margin Ge belt, the eastern upper Yangzi Ge belt, the northern Nanling Ge belt, the Huanjiang Ge belt, and the Nanling-Yunkai Ge belt.

Skarn-type and porphyry-type Ge mineralizations are distributed along the northern margin of the Yangzi Platform, the western margin of the Cathaysia Block, and the central and western sections of the Qinling-Qilianshan-Kunshan orogenic system, involving the Yangtze River mid-lower reaches Ge belt, the Nanling-Yunkai Ge belt, and the Qinling-Dabie-Xinghai Ge belt. In addition to the aforementioned Sichuan-Yunnan-Guizhou Ge-bearing belt and the middle and lower reaches of the Yangtze River Ge-bearing belt, sedimentary and volcanic Ge-rich deposits also include the North Qinling Ge-bearing belt and the Baluntai Ge-bearing belt. Aqueous sedimentary Ge deposits are concentrated in the Sichuan-Yunnan-Guizhou Ge-bearing belt and the Xiaoshanba Ge-bearing belt.

With increasing attention to Ge and continuous investment in its exploration, it is believed that more Ge mineralized areas and belts, and even independent Ge mineralized belts or deposits, will be discovered in mainland China.

6. Conclusions

The known associated/symbiotic Ge deposits in mainland China exhibit diverse genetic types, including endogenic igneous mesothermal-epithermal deposits, skarn-type, porphyry-type, and terrestrial and marine volcanic deposits. There are also aqueous

sedimentary deposits, such as organic coal-type Ge deposits, and inorganic bauxite and phosphate Ge deposits.

It is important to note that, in the context of Ge mineralization in this country, endogenic and exogenic sedimentary deposits are not independent or isolated, but rather exhibit mixed or combined mineralization.

Even within endogenic igneous Ge mineralization itself, each specific genetic type is not isolated but coexists and thrives. For example, porphyry, skarn, volcanic, and mesothermal-epithermal deposits, and even some exogenic sedimentary deposits, often occur together within the same tectonic-magmatic-sedimentary system, forming a relatively complete Ge metallogenic series. Therefore, finding one type of Ge mineralization in this area can lead to the discovery of other related types, improving prospecting efficiency.

Even organic coal-type Ge deposits are not formed in isolated, purely aqueous sedimentary formations, but are closely related to and/or connected with igneous activity. At the very least, igneous activity provides the ore source and/or ore-forming fluids and dynamics.

In terms of mineral types, Ge mineralization can be associated/symbiotic with many other metals such as Pb, Zn, Cu, Fe, W, Mn, Ag, and even non-metals such as S and P. Of course, among these associated/symbiotic minerals, coal and related sediments are also crucial.

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Data availability
The data that support the findings of this study are available from the author upon reasonable request.

Declaration of competing interest
The author declares that he has no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Use of AI tools declaration
The author declares that he has not used Artificial Intelligence (AI) tools in the creation of this article.